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INVESTIGATION OF PYROELECTRIC AND
PYROMAGNETIC DETECTION

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PYROMAGNETIC DETECTION

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by

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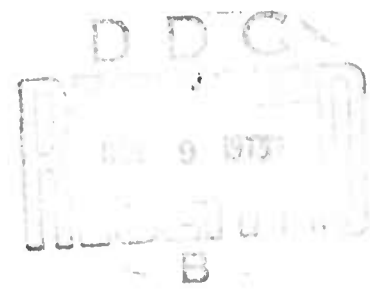
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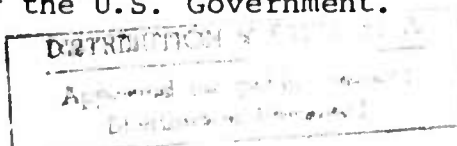
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FOREWARD

This investigation was conducted from July 1, 1973 to September 30, 1973 by the Department of Electrical Engineering, University of Minnesota, under Contract DAAK02-72-C-0398 monitored by Dr. P. McManigal, Advanced Research Projects Agency. The contracting officers representative is Mr. F. Petito, Night Vision Laboratory, Fort Belvoir, Virginia. The work was performed by A. van der Ziel, J.H. Judy, S.J. Lee, V. Singh and H.D. Park of the Electrical Engineering Department.

A. van der Ziel
Principal Investigator

SUMMARY

The capacitive bolometer effect must be described in terms of the d-c capacitance $C_d = Q/V$. The effect can also be interpreted as an induced pyroelectric effect.

The noise in d-c biased capacitive bolometers must be interpreted as polarization noise, enhanced by the d-c field.

The molecular field theory of ferroelectricity has been applied to the evaluation of p/ϵ and $p/(\epsilon)^{1/2}$. The first result holds independent of the model involved, whereas the second one depends upon the model. The calculated value of $p/(\epsilon)^{1/2}$ shows the right order of magnitude.

Extensive measurements were performed on capacitive bolometers. The results will be assembled in a special report.

The device manufacturing is concentrating on making new materials and on testing SBN devices.

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Introduction

In this report we give a survey of work performance under the contract for three areas.

- a) Theoretical work
 - b) Capacitive bolometer work
 - c) Materials preparation and testing
- a) The theoretical work consists of four parts:
- 1) Proof that the capacitive bolometer effect can be interpreted as an induced pyroelectric effect (submitted paper)
 - 2) Interpretation of the noise measurements of d-c biased capacitive bolometer in terms of polarization noise (submitted paper)
 - 3) Derivation of p/ϵ with the help of a generalized molecular field theory
 - 4) Derivation of p/ϵ for several molecular field theory models.
- The results agree reasonably well with experiment.
- b) The discussion of the capacitive bolometer work has been reserved for a special report.
- c) Our search for suitable pyroelectric and capacitive bolometer materials is continuing and so is our testing of these materials.

Part A. Theory

This section consists of 4 parts:

- 1) A paper on the capacitive bolometer effect, submitted to the J. Applied Physics. It shows that the capacitive bolometer effect is an induced pyroelectric effect. It also shows that the d-c capacitance $C_d = Q/V$ must be used in the discussion rather than the small-signal a-c capacitance $C = \partial Q / \partial V$.
- 2) A paper on noise in capacitive bolometers, submitted to the J. Applied Physics. The observed data are discussed in terms of polarization fluctuations.
- 3) A contribution of the generalized molecular field theory of pyroelectric detectors and capacitive bolometers. In it it is assumed that the polarization P depends on the local field E_l and the absolute temperature T as $P = f(E_l/T)$. This yields the figure of merit p/ϵ of the signal response of the pyroelectric detector and gives a general expression for the response of the capacitive bolometer.
- 4) A contribution to the molecular field theory of pyroelectric detectors for the classical and the two-level models. This yields an expression for $p/\epsilon^{1/2}$, which is a figure of merit for the NEP of the detector. Despite the crude models the results are within a factor 3 of the experimental data.

1. The Capacitive Bolometer Effect as an Induced Pyroelectric Effect*

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Summary: It is shown that the capacitive bolometer effect observed in ferroelectric capacitors can be considered as an induced pyroelectric effect. The capacitive bolometer interpretation is also correct, however, provided that the d-c capacitance, Q/V_0 rather than the small-signal a-c capacitance $\partial Q/\partial V_0$ is considered as the temperature dependent element.

*Supported by ARPA contract.

If a ferroelectric capacitor is irradiated by modulated radiation $P_1 \exp(j\omega t)$, and the capacitor has a heat capacitance C_H and a heat loss conductance g_H , then the temperature response of the capacitor is¹⁾, if η is the emissivity of the receiving surface

$$\Delta T(t) = \frac{\eta P_1}{j\omega C_H + g_H} \exp(j\omega t) \approx \frac{\eta P_1}{j\omega C_H} \exp(j\omega t) \quad (1)$$

The latter result is true if $\omega C_H > g_H$; this condition is satisfied for all modulation frequencies of practical interest.

There are now two ways of detecting this temperature variation:

- a) The pyroelectric mode. A poled ferroelectric capacitor of spontaneous polarization P_s gives, by the pyroelectric effect, rise to an output voltage¹⁾

$$V_d(t) = A \frac{\partial P_s / \partial T}{C_0} \Delta T(t) \quad (2)$$

Here A is the device area and C_0 the small-signal device capacitance. The device is then called a pyroelectric detector.

- b) The capacitive bolometer mode. An unpoled ferroelectric capacitor operating below the Curie temperature and not subject to irreversible domain wall motion (ferroelectric mode), or a ferroelectric capacitor operating above the Curie temperature (paraelectric mode) are used in the circuit of Fig. 1 where the load resistance is so chosen that $\omega C_0 R_L \gg 1$. The modulated radiation then produces a variation in device capacitance that is detected by the d-c voltage V_0 . The device is then called a capacitive bolometer.

To show this, we observe that the applied voltage V_o produces an induced polarization $P(V_o, T)$ and that the temperature $\Delta T(t)$ modulates this polarization. If A is the device area and $|\epsilon_o E| \ll |P|$, the charge Q in the capacitor is

$$Q = AP \quad (3)$$

The fluctuating short-circuit current is therefore

$$i_d(t) = \frac{\partial Q}{\partial t} = \frac{\partial Q}{\partial T} \cdot \frac{dT}{dt} = j\omega A \frac{\partial P}{\partial T} \Delta T \quad (3a)$$

according to Eq. (1). The fluctuating open-circuit voltage $V_d(t)$ is

$$V_d(t) = \frac{i_d(t)}{j\omega C_o} = \frac{A \partial P / \partial T}{C_o} \Delta T(t) \quad (4)$$

where C_o is the small-signal capacitance

$$C_o = \frac{\partial Q}{\partial V_o} = A \frac{\partial P}{\partial V_o} \quad (4a)$$

Comparing (4) and (2), we observe that the only difference is that the spontaneous polarization P_s has been replaced by the induced polarization P , so that the effect can indeed qualify as an induced pyroelectric effect.

To show that it can also qualify as a capacitive bolometer effect, we introduce the d-c capacitance

$$C_d = \frac{Q}{V_o} = \frac{AP}{V_o} \quad (5)$$

Equation (4) may then be written

$$V_d(t) = V_o \frac{\partial C_d / \partial T}{C_o} \Delta T(t) \quad (5a)$$

so that the effect can be interpreted as being caused by the temperature dependence of the d-c capacitance C_d . The distinction between C_d and C_o is crucial for the understanding of the operation of the device. It is, for example, in general not true that

$$v_d(t) = v_o \frac{\partial C_o / \partial T}{C_o} \Delta T(t) \quad (5b)$$

as has been suggested before.^{2,3)}

For low bias voltages P is proportional to V_o , so that C_d is independent of V_o . Therefore

$$C_o = \frac{\partial Q}{\partial V_o} = C_d = \text{constant} = C_{oo}(T) \quad (6)$$

and Eq. (5b) is correct. For that case the response is linear in V_o . At high voltages this is not the case; saturation effects set in and Eqs. (5a) or (4) must be used. Figure 2 gives the response of a TGS capacitor operated in the paraelectric mode: it shows both the linear regime and the saturation effect.

In the case of a ferroelectric capacitor with irreversible domain wall motion hysteresis effects occur, so that $P(V_o, T)$ is no longer a unique function of V_o but depends on past history. Nevertheless, at a given operating condition C_d and C_o exist so that Eq. (5a) remains valid.

It is also possible to express $v_d(t)$ in terms of derivatives of $P(V_o, T)$ substituting (4a) into (4) yields

$$v_d(t) = \frac{\partial P / \partial T}{\partial P / \partial V_o} \Delta T(t) \quad (7)$$

so that the response can be calculated as soon as $P(V_o, T)$ is known. We are presently looking into the problem of evaluating this function.

Since the pyroelectric response and the capacitive bolometer response are governed by the same equation, it is not possible to separate an observed effect in the ferroelectric regime into a pyroelectric and a capacitive bolometer part, as Cooper tried to do.⁴⁾

References

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2. Polarization Fluctuations in Capacitive Bolometers*

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Summary

The noise resistance R_n of an a-c open-circuited capacitive bolometer is measured as a function of the d-c bias. It is found that the noise is larger than thermal noise and that the ratio R_n/R_s , where R_s is the loss series resistance of the device, increases with increasing bias and saturates for large bias. The observations are discussed in terms of spontaneous polarization fluctuations for a bias field.

*Supported by ARPA contract.

We have measured the noise resistance $R_n(E)$ of an a-c open-circuited TGS capacitive bolometer operating at $T > T_c$ as a function of the d-c field E at 1 KHz and have compared the result with the series loss resistance $R_s(E)$ of the bolometer at the same bias. If the noise were thermal noise, we would have

$$R_n(E) = R_s(E) \quad (1)$$

We found this result at zero bias, but for larger bias $R_n(E) > R_s(E)$ and $R_n(E)$ saturates for large fields. Figures 3 and 4 show the results.

Figure 1 shows R_n and R_s measured at a relatively large value of $T - T_c$. The saturation effect is clearly seen, and R_s is independent of the applied field.

Figure 2 shows R_n and R_s measured for a relatively small value of $T - T_c$. We now see that R_s increases with increasing bias, but that R_n increases more strongly, and again saturates at larger field strengths.

R_s was determined from bridge measurements by determining the capacitance C and the loss tangent, $\tan \delta$, at the operating bias. We found for relatively small values of $T - T_c$ that C decreases and $\tan \delta$ increases with increasing bias. R_s then follows from

$$R_s = \frac{\tan \delta}{\omega C} \quad (2)$$

In a short circuited device with a bias voltage V_0 applied (Fig. 1) the charge Q in the capacitor may be written

$$Q = (\epsilon_0 E + P)A \text{ and; } I = \frac{dQ}{dt} \quad (3)$$

Here P is the polarization, A the device area and I the current. Since E is now kept constant, a fluctuation in I must come from fluctuations in P . This points to spontaneous polarization fluctuations as the only source of noise.

It is well known for a material with a relative dielectric constant $\epsilon = \epsilon' - j\epsilon''$ under equilibrium conditions that Nyquist's theorem can be expressed in terms of polarization fluctuations with a spectrum¹

$$S_p^A(f) = \frac{4kT\epsilon_0\epsilon''}{\omega Ad} \quad (4)$$

where d is the electrode distance. If under applied field the device would still show thermal noise, we would have instead

$$S_p(f) = \frac{4kT\epsilon_0\epsilon''(E)}{\omega Ad} \quad (5)$$

where the imaginary part ϵ'' of the dielectric constant may now depend upon field. But actually the noise should be larger than thermal noise, so that we may write

$$S_p(f) = \frac{4kT\epsilon_0\epsilon''(E)}{\omega Ad} g(E) \quad (6)$$

where $g(E)$ is a function of E that is unity at zero bias and larger than unity for $E \neq 0$.

Just as Eq. (5) leads to an open-circuit noise voltage with a spectrum

$$S_v(f) = 4kT R_s(E) \quad (7)$$

so Eq. (6) will lead to an open-circuit noise voltage with a spectrum

$$S_v(f) = 4kT R_s(E) g(E) = 4kT R_n(E) \quad (8)$$

Consequently

$$g(E) = \frac{R_n(E)}{R_s(E)} \quad (9)$$

so that the function $g(E)$ is experimentally determined from the measurement of $R_s(E)$ and $R_n(E)$. We have not yet been able to evaluate the function $g(E)$ theoretically.

References

1. R.E. Burgess, Can. J. Physics 36, 1569, 1958, J.J. Biophy, Fluctuations in Magnetic and Dielectric Solids, in R.E. Burgess, Ed., Fluctuation Phenomena in Solids, Academic Press, New York, 1965, pp. 1-34.

3. Generalized Molecular Field Theory of the Pyroelectric Effect and Capacitive Bolometer Effect

In the pyroelectric effect the significant parameter is p/ϵ , or, if $\epsilon \gg 1$, we may write

$$\frac{p}{\epsilon} \approx \left(\frac{p}{\epsilon-1} \right) = \epsilon_0 \frac{\partial P / \partial T}{\partial P / \partial E} \quad (1)$$

where $p = \partial P / \partial T$ is the pyroelectric coefficient and $P = P_s$, whereas

$$\epsilon-1 = \frac{1}{\epsilon_0} \frac{\partial P}{\partial E}.$$

In the capacitive bolometer of electrode distance d

$$v_d(t) = \frac{\partial P / \partial T}{\partial P / \partial V_0} \Delta T = d \frac{\partial P / \partial T}{\partial P / \partial E} \Delta t(t) \quad (2)$$

since $E = V_0/d$. Both problems thus have in common that the quantity of interest is

$$\frac{\partial P / \partial T}{\partial P / \partial E} \quad (3)$$

To evaluate this expression, we assume that the polarization P is a function $f(E_l/T)$ of the local field E_l , where T is the absolute temperature,

$$E_l = E + \frac{\lambda P}{\epsilon_0} \quad (4)$$

and λ is a kind of Lorentz factor. We thus have

$$P = f(E_l/T) = f\left(\frac{E + \lambda P / \epsilon_0}{T}\right) \quad (5)$$

The function f need not be further specified at the moment.

We call this the generalized molecular field theory of the effects.

If f' denotes the derivative, we have

$$\frac{\partial P}{\partial T} = f' \left[-\frac{(E + \lambda P / \epsilon_0)}{T^2} + \frac{\lambda}{\epsilon_0 T} \frac{\partial P}{\partial T} \right]$$

or

$$\frac{\partial P}{\partial T} = - \frac{f'}{(1 - f' \lambda / \epsilon_0 T)} \left(\frac{E + \lambda P / \epsilon_0}{T^2} \right) \quad (6)$$

$$\frac{\partial P}{\partial E} = f' \left[1 + \frac{(\lambda / \epsilon_0) \partial P / \partial E}{T} \right]$$

or

$$\frac{\partial P}{\partial E} = \left(\frac{f'}{1 - f' \lambda / \epsilon_0 T} \right) \frac{1}{T} \quad (7)$$

Therefore

$$\frac{\partial P / \partial T}{\partial P / \partial E} = - \frac{E + \lambda P / \epsilon_0}{T} \quad (8)$$

We thus see that the explicit form of f is not important; all that matters is that it is a function of $\left(\frac{E + \lambda P / \epsilon_0}{T} \right)$

We now turn to the pyroelectric effect. Here $E=0$ and $P=P_s$. Hence

$$\frac{P}{\epsilon - 1} = \epsilon_0 \left(\frac{\lambda P_s / \epsilon_0}{T} \right) = - \frac{\lambda P_s}{T} \quad (9)$$

This is generally valid as long as (5) is valid.

We must now get rid of λ . To that end we consider $T > T_c$ but close to T_c and assume E to be small. Then P is a linear function of E ,

$$P = a \epsilon_0 \epsilon_l = a \frac{(\epsilon_0 E + \lambda P)}{T} \quad (10)$$

where a is a constant that needs to be expressed in measurable parameters

$$P(1 - \frac{a\lambda}{T}) = \frac{a\epsilon_0 E}{T}, \text{ or } P = \frac{a\epsilon_0 E}{T - a\lambda} \quad (11)$$

But we know that in this case

$$\frac{P}{\epsilon_0 E} = \frac{C}{T - T_c} \quad (12)$$

where C is Curie's constant and T_c is the Curie temperature. Therefore

$$T_c = a\lambda \quad a = C, \text{ or } \lambda = \frac{T_c}{C} \quad (13)$$

Hence

$$\frac{p}{\epsilon - 1} = - \frac{T_c}{T} \frac{P_s}{C} \quad (14)$$

A similar relationship was first found by S.T. Liu¹, derived for $T \simeq T_c$, and consequently the factor T_c/T was missing. The factor is important, however, for devices with a high Curie temperature; they should have a higher value of $p/(\epsilon - 1)$ at room temperature.

We now turn to the capacitive bolometer effect for $T > T_c$.

Since $\lambda P \gg \epsilon_0 E$, we have

$$\frac{\partial P / \partial T}{\partial P / \partial E} \simeq \frac{\lambda P / \epsilon_0}{T}$$

so that

$$v_d(t) = - \frac{\lambda d}{\epsilon_0 T} P \Delta T(t) \quad (15)$$

This equation is generally valid as long as $\epsilon_0 E \ll P$.

We now assume E to be small. Then P varies linearly with E and, according to (11)

$$v_d(t) = - \frac{\lambda d}{\epsilon_0 C} \left(\frac{\epsilon_0 EC}{T - T_c} \right) \Delta T(t) = \left(\frac{V_0}{T - T_c} \right) \Delta T(t) \simeq -V_0 \frac{\Delta T(t)}{T - T_c} \quad (16)$$

in agreement with previous results. The response is then linear in V_0 . For large values of V_0 the response $v_d(t)$ saturates. This must come about because the polarization P in (15) saturates. Experimentally $|V_d(t)|_{\text{sat}}$ increases strongly with decreasing $T-T_c$; this then must mean that the saturated value for P increases strongly with decreasing $T-T_c$. This can only be verified theoretically if the function $f(-\frac{E+\lambda P/\epsilon_0}{T})$ is further specified.

References:

1. S.T. Liu, Evaluation of Curie Constants of Ferroelectric Crystals from Pyroelectric Response, Presented at 3^d International Meeting on Ferroelectricity, Edinburgh, Scotland, Sept. 10-14, 1973.

4. Molecular Field Theory of Ferroelectricity and its Application

In the preceding section we discussed the case that the polarization $P(T)$ was an arbitrary function of E_l/T where $E_l = E + \lambda P/\epsilon_0$ is the local field, λ the Lorentz factor, T the absolute temperature and E the applied field. We were then able to give a generally valid expression for $p/(\epsilon-1)$, where p is the pyroelectric coefficient and ϵ the relative dielectric constant; $p/(\epsilon-1)$ is a figure of merit for the signal response of a pyroelectric detector.

In the expression for the noise equivalent power another figure of merit must be introduced; it is $p/(\epsilon-1)^{1/2}$. It is therefore necessary to give a general expression for $p/(\epsilon-1)^{1/2}$. In contrast to the previous case, explicit expressions for the function of (E_l/T) must now be used.

To that end we assume that each molecule has a permanent electric moment μ . There are now several possibilities:

a) The dipoles can orient themselves in arbitrary directions (classical approach). This leads to the following expression for the polarization

$$P(T) = P(o)L(x); L(x) = \coth x - \frac{1}{x}; x = \frac{\mu E_l}{kT} \quad (1)$$

where $P(o) = N\mu$ is the total polarization when all dipoles are aligned. μ the dipole moment, N the number of dipoles per unit

volume, k = Boltzmann's constant. This gives the classical molecular field theory of ferroelectricity.

b) There are several preferred directions of polarization. The simplest case is that the dipoles can orient themselves parallel or antiparallel a preferred direction. In that solution

$$P(T) = P(0) \tanh x. \quad (2)$$

This is the two-level molecular field theory of ferroelectricity.

It should, of course, be understood that more complicated directions of polarization are possible. For example, in BaTiO_3 these are the parallel, antiparallel and perpendicular directions; of the latter there are four equivalent orientations. Therefore the total number of orientations is 6, corresponding to two preferred directions along each cubic axis.

By solving Eqs. (1) and (2) for $E=0$, one obtains $P/P(0)$ as a function of T . Graphically this is done in Fig. 5, from which we see that the line $P(T)/P(0) = a(T)x$ meets the curve $L(x)$ or $\tanh(x)$.

We see that there are two possibilities for properly chosen values of T :

a) The two curves meet at a non-zero value of x , and hence of $P(T)$. In other words we have spontaneous polarization. This is called the ferroelectric regime.

b) The two curves intersect at $x=0$ only. Hence $P(T)=0$, so that we have no spontaneous polarization. This is called the paraelectric regime.

c) In between there is a temperature $T=T_c$ where the line $P(T)/P(0) = a(T)x$ is tangent to $L(x)$ or $\tanh x$ at $T=0$. This is called the Curie temperature.

Figure 6 shows $P_s(T)/P(0)$ plotted versus T_c/T for the classical and for the two-level theory. Also shown are measured points for TGS, matched at $T/T_c = 0.88$.

Besides the classical and the two-level theories there is also the thermodynamic theory which assumes E to be a non-linear function of the polarization P .

Since P changes sign if E changes sign, E must be an odd function of P . The thermodynamic theory of ferroelectricity thus writes

$$E = \beta(T-T_c)P + bP^3 + \dots \quad (3)$$

We then see that for $T < T_c$ this gives spontaneous polarization P_s for $E = 0$. This yields

$$\beta(T-T_c) + bP_s^2 = 0 \quad P_s = \left[\frac{\beta}{b}(T_c-T)\right]^{1/2} \quad (4)$$

$$p = \frac{\partial P}{\partial E} = -\left(\frac{\beta}{b}\right)^{1/2} \frac{1}{(T_c-T)^{1/2}} \quad (5)$$

$$\epsilon-1 = \frac{1}{\epsilon_0 \frac{\partial E}{\partial P}} = \frac{1/\epsilon_0}{\beta(T-T_c) + 3bP_s^2} = \frac{1/\epsilon_0}{2\beta(T_c-T)} \quad (6)$$

Consequently

$$\frac{P}{\epsilon-1} = -\frac{1}{2} \left(\frac{\beta}{b}\right)^{1/2} (2\beta\epsilon_0)^{1/2} = -\beta \left(\frac{\epsilon_0}{2b}\right)^{1/2} \quad (7)$$

In order to evaluate this expression we must evaluate β and

b. We do this for the two models described by Eqs. (1) and (2).

We first discuss the classical case described by Eq. (1).

For small values of x the equation may be written as

$$\frac{P(T)}{P(0)} = \frac{1}{3} x - \frac{1}{45} x^3 + \dots \quad (8)$$

Suppose x is quite small, $E \neq 0$ and T is sufficiently large. We then have

$$P = \frac{1}{3} P(0) x = \frac{1}{3} \frac{N\mu^2}{kT} \left[E + \frac{\lambda P}{\epsilon_0} \right] \quad (9)$$

$$\text{or } P(T) \left[1 - \frac{1}{3} \frac{N\mu^2 \lambda}{\epsilon_0 kT} \right] = \frac{1}{3} \frac{N\mu^2}{kT} E$$

$$P(T) = \frac{\frac{1}{3} N\mu^2 / (\epsilon_0 k)}{T - T_C} \epsilon_0 E = \frac{C}{T - T_C} \epsilon_0 E \quad (10)$$

where

$$T_C = \frac{N\mu^2 \lambda}{3 \epsilon_0 k}, \quad C = \frac{1}{2} \frac{N\mu^2}{\epsilon_0 k} = \frac{T_C}{\lambda} \quad (10a)$$

T_C is the Curie temperature and C is called the Curie constant.

The derivation holds for $T > T_C$. For $T < T_C$ spontaneous polarization occurs; this must be discussed separately.

We can invert Eq. (8) as follows

$$x = 3 \frac{P}{P(0)} + \frac{9}{5} \left[\frac{P}{P(0)} \right]^3 + \dots \quad (11)$$

$$\text{or } E + \frac{\lambda P}{\epsilon_0} = \frac{3kT}{2N\mu} P + \frac{9}{5} \left[\frac{P}{P(0)} \right]^3 + \dots$$

since $P(0) = N\mu$, so that

$$E = \left(\frac{3kT}{2N\mu} - \frac{\lambda}{\epsilon_0} \right) P + \frac{9}{5} \frac{kT}{N^3 \mu^4} P^3 + \dots \quad (12)$$

This is of the form (3), and

$$\beta = \frac{3k}{2 N \mu}, \quad b = \frac{9}{5} \frac{kT}{N^3 \mu^4} \quad (13)$$

Consequently

$$\frac{P}{(\epsilon-1)^{1/2}} = \frac{3k}{2 N \mu^2} \left(\frac{\epsilon_0}{2} \frac{5N^3 \mu^4}{gkT} \right)^{1/2} = \left(\frac{5}{2} \epsilon_0 \frac{Nk}{T} \right)^{1/2} \quad (14)$$

Next we discuss the two-level case. For small values of x , Eq.

(2) may be written

$$\frac{P(T)}{P(0)} = x - \frac{1}{3} x^3 + \dots \quad (15)$$

Suppose x is quite small, $E \neq 0$ and T sufficiently large. We then have

$$P = P(0)x = \frac{N\mu^2}{kT} \left(E + \frac{\lambda P}{\epsilon_0} \right) \quad (16)$$

$$\text{or } P \left[1 - \frac{N\mu^2 \lambda}{\epsilon_0 kT} \right] = \frac{N\mu^2}{kT} E$$

so that

$$P(T) = \frac{N\mu^2 / \epsilon_0 k}{T - T_c} \epsilon_0 E = \frac{C}{T - T_c} \epsilon_0 E \quad (17)$$

where T_c is the Curie temperature and C the Curie constant

$$T_c = \frac{N\mu^2 \lambda}{\epsilon_0 k}; \quad C = \frac{N\mu^2}{\epsilon_0 k} = \frac{T_c}{\lambda} \quad (17a)$$

This derivation holds again for $T > T_c$; spontaneous polarization occurs for $T < T_c$; this must again be discussed separately.

The two models thus differ in the values of T_c and C ; in the classical case T_c and C are a factor 3 smaller than in the two-level case.

We can invert Eq. (15) as follows

$$x = \frac{P}{P(0)} + \frac{1}{3} \left[\frac{P}{P(0)} \right]^3 + \dots \quad (18)$$

$$\text{or } E + \frac{\lambda P}{\epsilon_0} = \frac{kT}{2 \mu N} P + \frac{kT}{3 \mu N^3} P^3 + \dots$$

so that

$$E = \left(\frac{kT}{2 \mu N} - \frac{\lambda}{\epsilon_0} \right) P + \frac{kT}{3 \mu N^3} P^3 + \dots \quad (19)$$

This is of the form (3) so that

$$\beta = \frac{k}{2 \mu N} ; \quad b = \frac{kT}{3 \mu N^3} \quad (20)$$

Consequently

$$\frac{P}{(\epsilon-1)^{1/2}} = \frac{k}{2 \mu N} \left(\frac{\epsilon_0}{2} \frac{3 \mu N^3}{kT} \right)^{1/2} = \left(\frac{3}{2} \epsilon_0 \frac{Nk}{T} \right)^{1/2} \quad (21)$$

This differs from (14) only by a factor $(5/3)^{1/2} = 1.29$; this difference between the two models is relatively small.

We should make one correction for our results given in Eqs. (14) and (21). The derivations are only correct relatively close to the Curie temperature T_c . Therefore, it is perhaps better to replace T by T_c in Eqs. (14) and (21). We then have: Classical Theory:

$$\frac{P}{(\epsilon-1)^{1/2}} \left(\frac{5}{2} \epsilon_0 \frac{Nk}{T_c} \right)^{1/2} \quad (22)$$

Two level theory:
$$\frac{P}{(\epsilon-1)^{1/2}} = \left(\frac{3}{2} \epsilon_0 \frac{Nk}{T_c}\right)^{1/2} \quad (23)$$

We must now find the suitable expression for N, the density of dipoles. It is easily seen that

$$N = \frac{A\rho}{W} \quad (24)$$

where A is Avagadro's number, ρ is the density and W the molecular weight. Evaluating the numbers we have

$$\frac{P}{(\epsilon-1)^{1/2}} = 13.5 \times 10^{-9} \left(\frac{\rho}{\frac{W}{100} \cdot \frac{T_c}{100}}\right)^{1/2} \frac{\text{Coulomb}}{\text{cm}^2 \text{ } ^\circ\text{K}} \quad (25)$$

for the classical theory and

$$\frac{P}{(\epsilon-1)^{1/2}} = 10.5 \times 10^{-9} \left(\frac{P}{\frac{W}{100} \cdot \frac{T_c}{100}}\right)^{1/2} \frac{\text{Coulomb}}{\text{cm}^2 \text{ } ^\circ\text{K}} \quad (25a)$$

The results obtained are shown in Table I for Eq. (25)

Table I

Material	$\epsilon(20^\circ\text{C})$ (exp)	$p(20^\circ\text{C})$ (exp)	$p/(\epsilon-1)^{1/2}$ (exp)	ρ	W	T_c	$P/(\epsilon-1)^{1/2}$ (calc)
TGS	40	2×10^{-8}	3.2×10^{-9}	1.69	323	322	5.5×10^{-9}
LiTaO ₃	46	2.4×10^{-8}	3.5×10^{-9}	7.50	234	900	8.1×10^{-9}
SBN(x=0.5)	400	2.4×10^{-8}	3.5×10^{-9}	5.33	394	380	8.1×10^{-9}
PLXT(x=0.65)	1400	11×10^{-8}	3×10^{-9}	7.82	324	45	9.8×10^{-9}

It is suspected that if p and ϵ were measured closer to T_c , the value of $p/(\epsilon-1)^{1/2}$ would be closer to the value predicted by Eq. (25).

We have also expanded E versus P to higher order terms; one then obtains correction factors for $p/(\epsilon-1)^{1/2}$ that become significant farther away from the Curie temperature T_c . The changes, though significant, are not very large.

Table I was constructed under the assumption that a dipole unit consists of 1 molecule. This is probably not the case for some structures. If n molecules form one dipole, the effective molecular weight is n times as large. The calculated value of $p/(\epsilon-1)^{1/2}$ could thus lie closer to the experimental value. This must be checked with the actual structure of the material.

It should also be noted that $p/(\epsilon-1)^{1/2}$ is a factor 1.29 smaller for the two-level theory. This theory would thus bring the value for TGS down to 4.3×10^{-9} Coulomb per cm^2 per $^\circ\text{K}$, which is quite close.

It should also be noted that $p/(\epsilon-1)^{1/2}$ does not depend on $T-T_c$. Little is therefore gained by operating closer to the Curie temperature. Also $p/(\epsilon-1)^{1/2}$ does not depend very strongly upon the material, in agreement with experiment.

The final conclusion is therefore that the calculated value of $p/(\epsilon-1)^{1/2}$ gives the right order of magnitude, and that closer agreement might be obtained by further refinements of the theory.

/s/ by S.T. Liu

Part B. Materials Research

1) Work in the Chemistry Department

This section has concerned itself with the preparation of new samples of materials of high dielectric constant for noise studies and for devices, including the capacitive bolometer. During this period the samples prepared were polycrystalline; we mention later work toward single crystal samples. A large number of samples have been prepared with the intent of obtaining Curie temperatures above 25°C. We have had considerable success in using induction heating of samples in a graphite susceptor in an argon atmosphere. We have dealt most extensively with mixed titanates and stannates or stannate-titanate combinations. These have been sintered at 1450°C after having been compressed into pellets at 20,000 psi. The reducing atmosphere represented by heating in a graphite susceptor typically leads to an oxygen deficiency in these complex oxides. If one were to work toward a precisely defined stoichiometry one might heat in the carbon monoxide-carbon dioxide mixture appropriate to the desired equilibrium partial pressure of oxygen. However, we have found it sufficient for purposes of preparing samples with good pyroelectric properties to heat in air or in one atmosphere of oxygen.

A considerable improvement which we have made use of recently uses a graphite susceptor totally enclosed in silica. We have used spectroscopic-type graphite rods machined with a cup on top. The fused silica envelope has a corresponding cup to serve as retainer

for a small alumina or porcelain crucible. Prior to the sealing off, the graphite is extensively outgassed in vacuum at a temperature higher than that to which it will be subjected in the susceptor. This procedure makes it possible to do the heating in air. Thus far we have been cautious about heating in oxygen, in the event that a crack might occur in the silica envelope and expose the very hot carbon to oxygen. Our first susceptor developed a small internal arcing problem which we hope to rectify.

Some of the studies of electrical characteristics would be made far more meaningful by using single crystals. The requirement for pyroelectric behavior that the crystal not have a center of symmetry implies that the electrical properties are anisotropic. In many cases there is one crystal axis of extremely high dielectric constant. We are engaged in modifying existent crystal-pulling equipment to permit the growing of mixed oxides.

2) Work in the EE Department

- a) The calibrated 500°K signal source was compared with the one used by Honeywell and good agreement was noted.
- b) Samples of SBN were obtained from Harshaw Chemical Co. They are being contacted in various ways (burned silver, burned gold, evaporated gold-chromium contact) poled, and compared for signal response and D^* .
- c) Extensive work has been done on the d-c and a-c capacitive bolometer. Mr. V.P. Singh is writing a Ph.D. thesis on the subject that will be issued as a special report before Dec. 31, 1973.

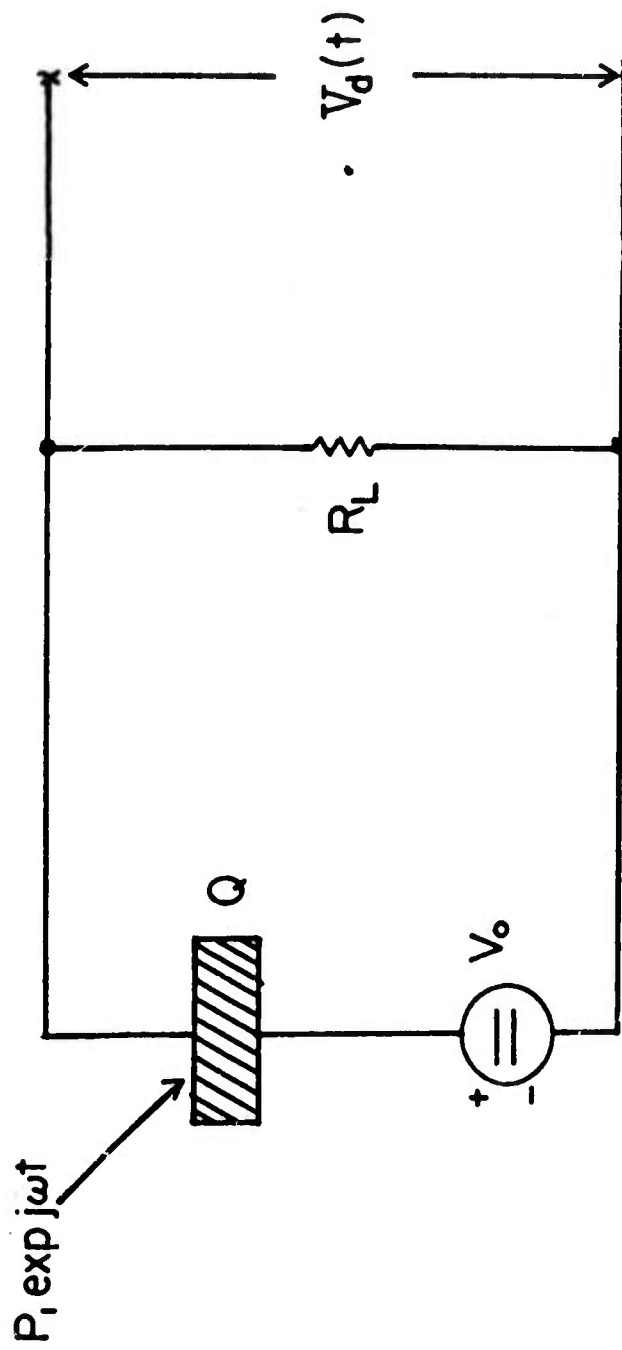


FIG. 1 D-C bolometer circuit

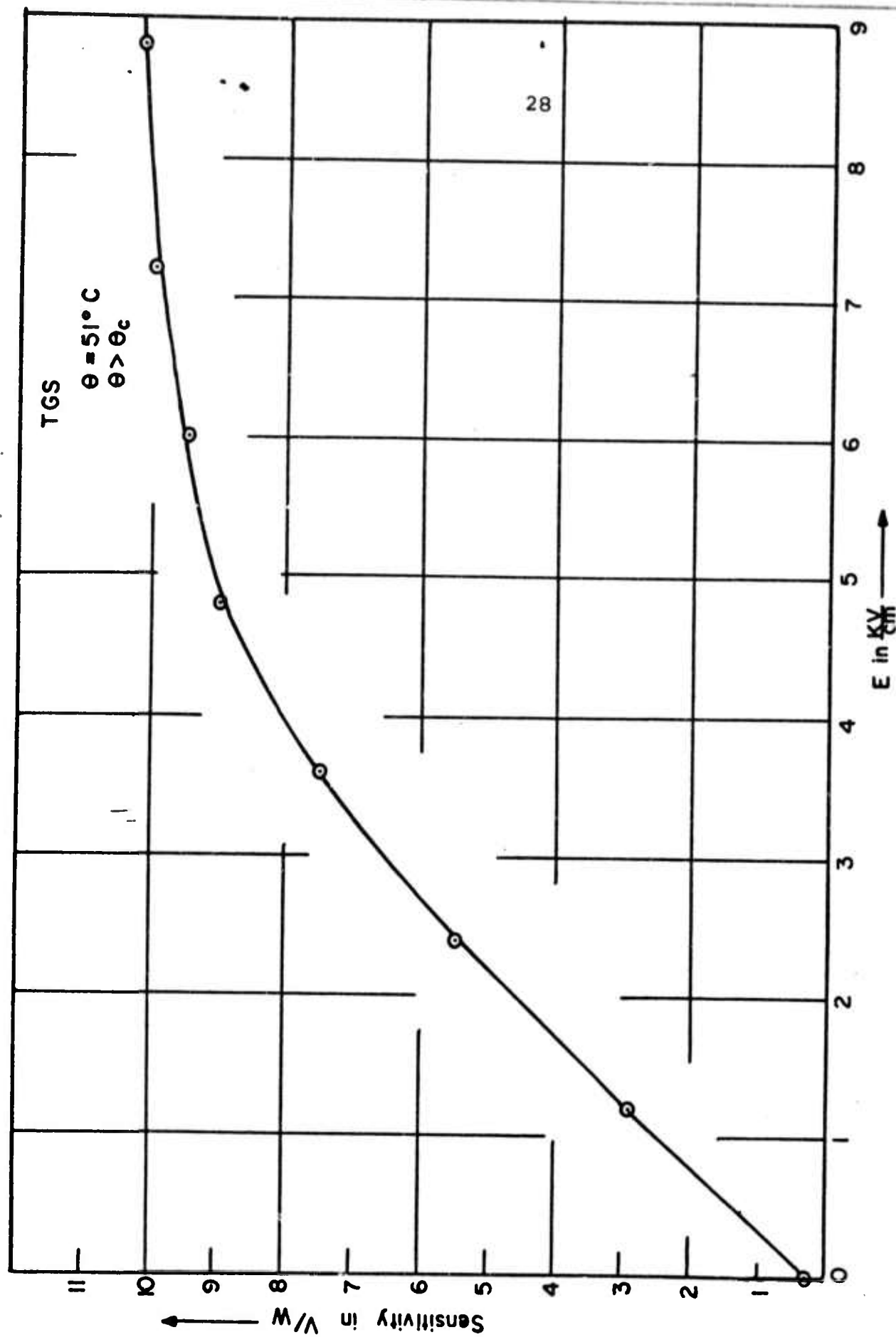


FIG. 2 Capacitive bolometer sensitivity in volts/watts versus applied field in kvolts/cm.

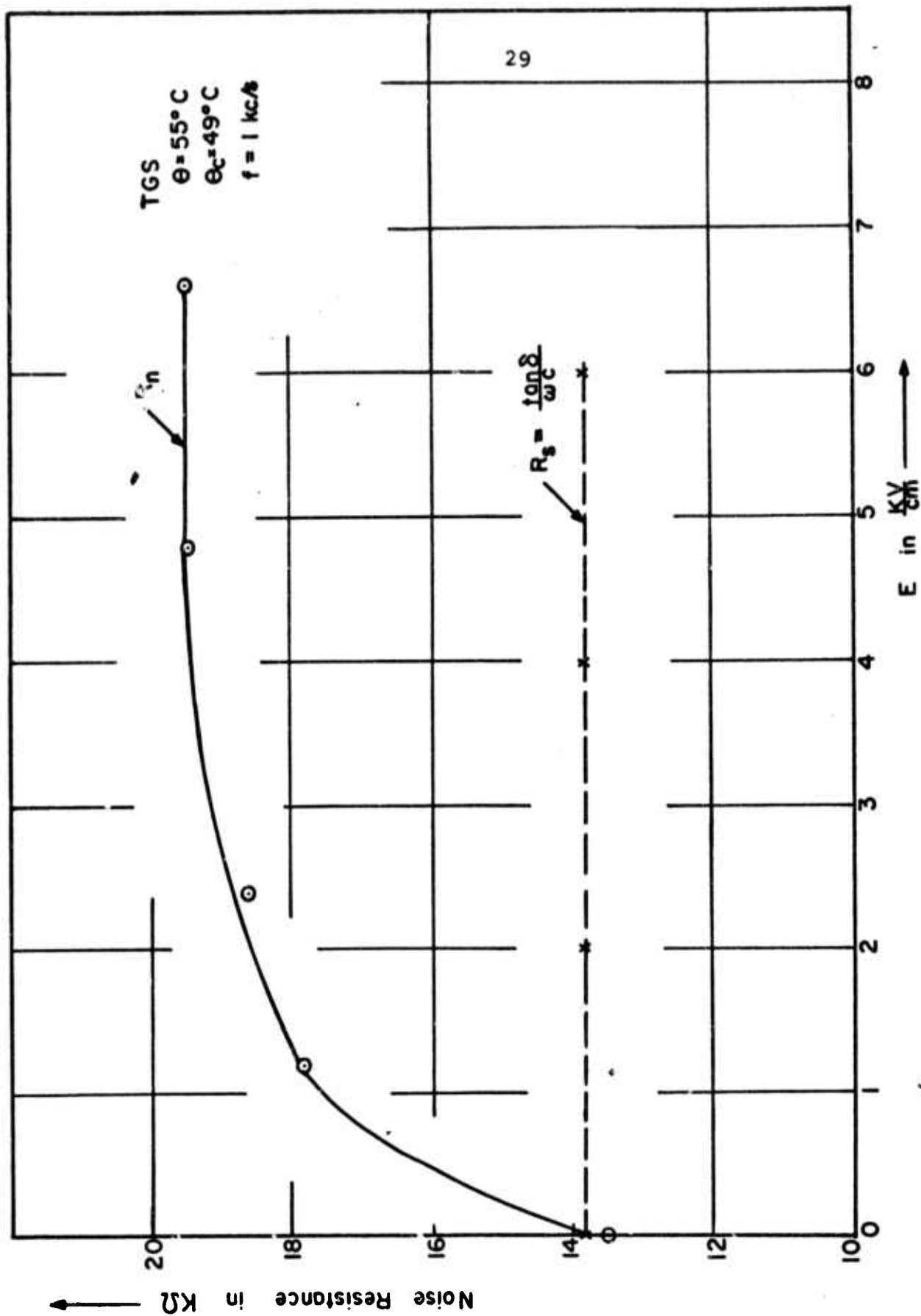


Figure 3 Equivalent noise resistance of TGS versus applied field at $T - T_c = 6^\circ \text{C}$.

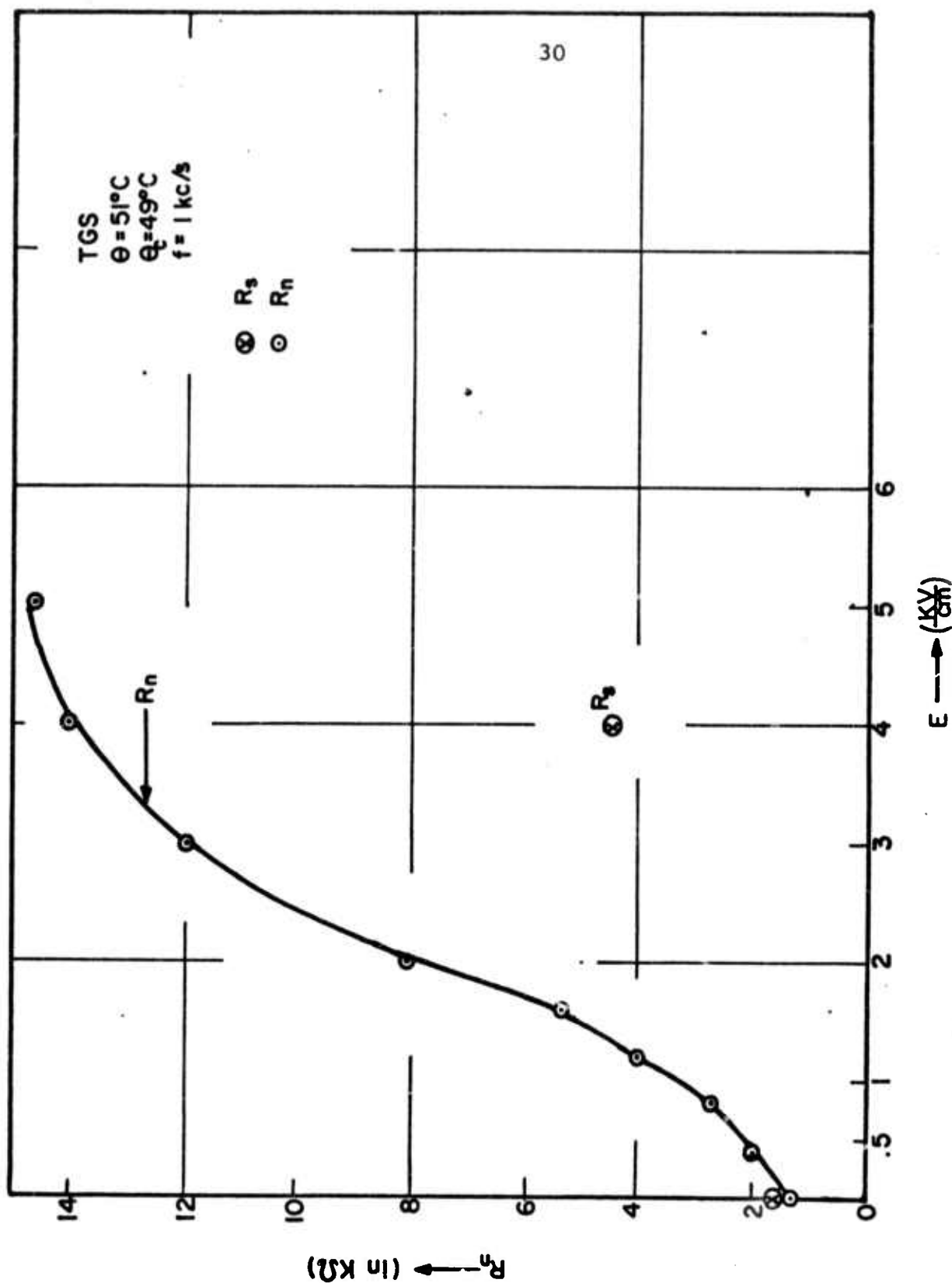


Figure 4 Equivalent noise resistance of TGS versus applied field at $T - T_c = 2^\circ\text{C}$.

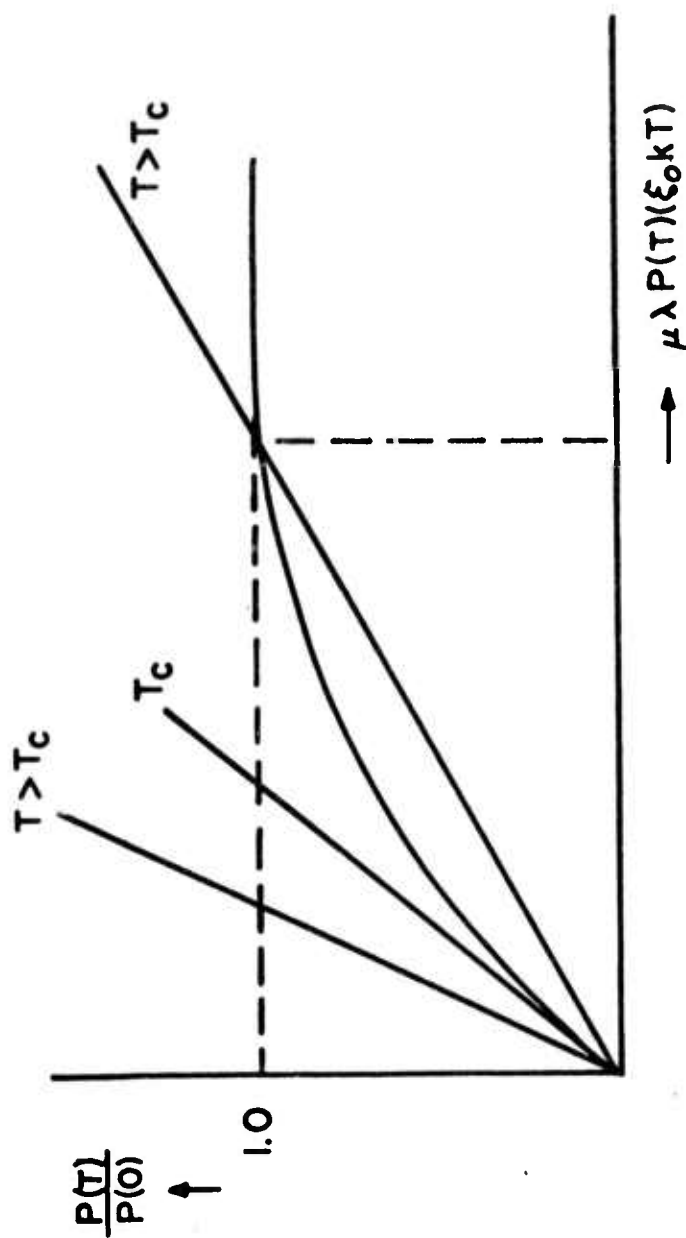


FIG. 5

Graphical determination of the saturation polarization, if any.

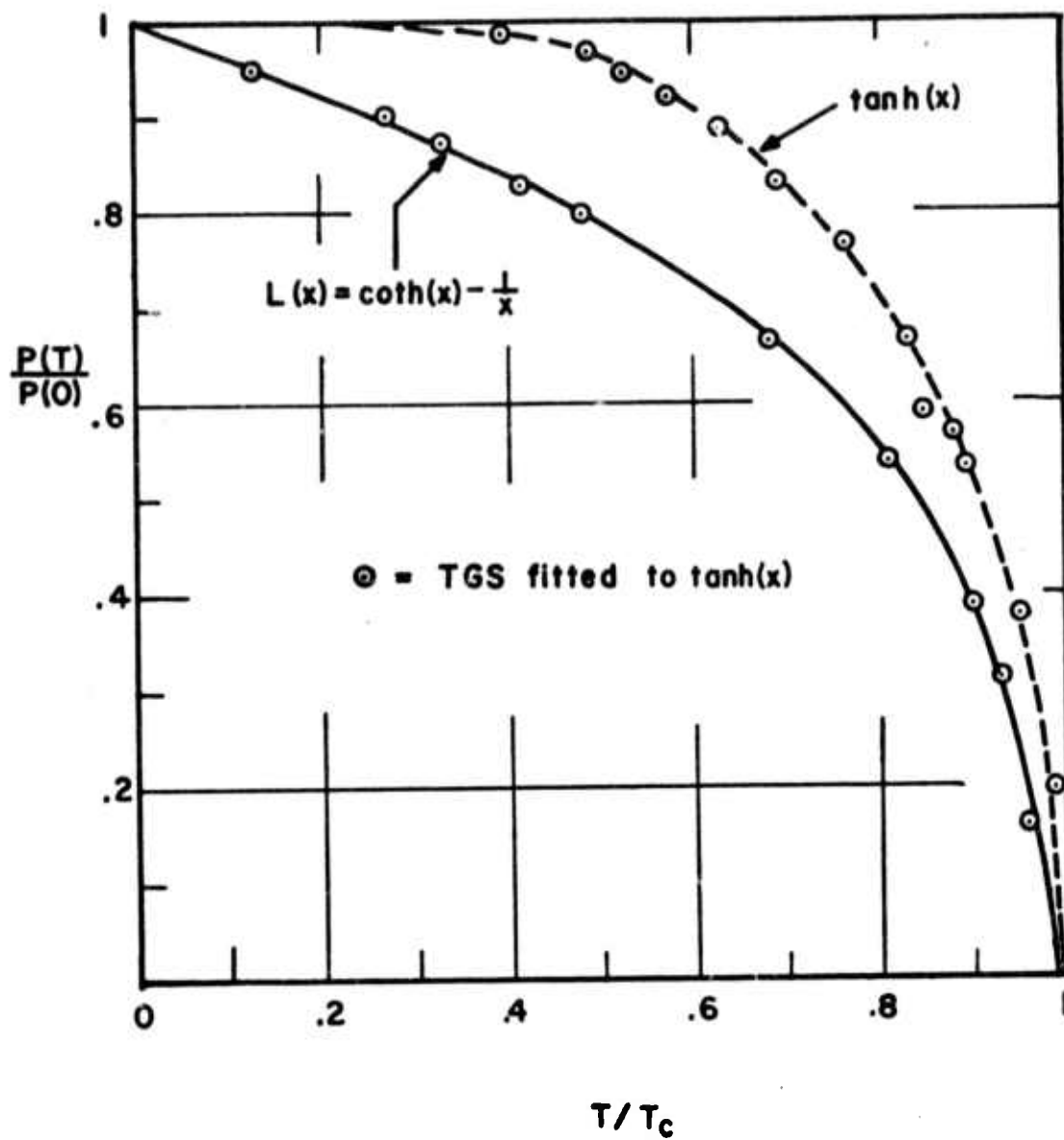


FIG. 6

$P_s(t)/P(0)$ plotted versus T/T_c for the classical and the two-level cases.